

# Influence of Carbon Quantum Dots on the Electrical Performance of Triboelectric Generators <sup>†</sup>

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**Abstract:** In this work we investigate the triboelectric properties of Carbon Quantum Dots (CQDs) films for potential application in triboelectric generators. CQDs were deposited on silicon wafers, using spin on techniques. Device performance was estimated in sliding mode experiments, where the CQDs-surface was sliding on top of a flexible substrate. The triboelectric signal as well as the charging of capacitors, after signal rectification, was monitored as a function of time. Our results indicate that surface roughness plays a very important role in the triboelectric signal and could compensate opposite trends due to other parameters, such as the dielectric film thickness.

**Keywords:** triboelectricity; triboelectric generator; carbon dots; surface roughness; energy harvesting

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## 1. Introduction

Today’s society is facing a major challenge, that of finding a new energy source to cover its needs. Despite the fact that the needs grow bigger, it is well known that the reserve of fossil fuels is constantly diminishing. Furthermore, the technological development in the last decades, resulted to the elaboration of self-powered electronic systems, sensor networks and the rise of the Internet-ofThings (IoT). The basic requirements of those wireless systems are that their units operate autonomously and sustainably. Thus, it is highly desirable to integrate these systems with an energy harvester that can utilize the ambient energy of the environment and form an ideal self-powered system. That was the idea behind the birth of nanogenerators which can harvest energy in the micropower regime.

Scavenging of mechanical energy has been gaining ground world-wide. Triboelectricity has been rapidly emerging as a powerful technology for converting the abundant mechanical energy of the ambient environment to electrical energy. As a result triboelectric generators (TEGS) have been already reported for a vast number of applications ranging from small scale, suitable for IoT and portable electronics to large scale, for satisfying domestic energy consumption [1]. TEGS operate on the principle of coupling the triboelectric effect and the electrostatic induction between the surfaces of two dissimilar materials. When the materials come to physical contact, triboelectric charges appear on the two surfaces. Subsequently, with the separation of the two surfaces due to an external mechanical force, a potential drop is generated, driving the electron flow between the two electrodes

built on the top and the bottom of the two materials. By deploying this mechanism, TEGs can be applied to harvest the mechanical energy and convert it to electrical.

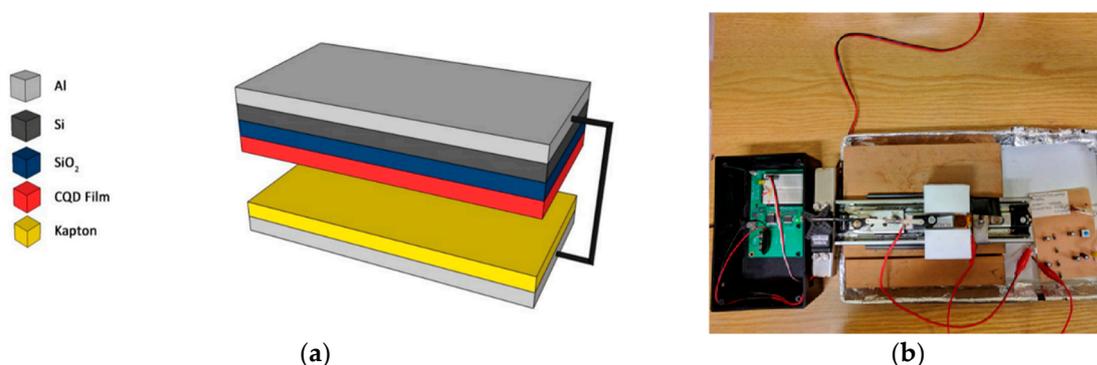
Triboelectric generators emerge as a new technology with numerous advantages, including high efficiency, low cost and high adaptability. They can generate electricity from any type of mechanical motions such as impact and vibration and are also able to serve as self-powered active sensors. Aiming to achieve enhanced charge transfer and therefore improved performance of the triboelectric generators, a variety of materials as well as surface structuring strategies have been investigated in order to modify the topography and properties of the contacting surfaces [2]. To this extent, in this work we investigate the triboelectric properties of Carbon Quantum Dot (CQD) films for potential application in triboelectric generators.

## 2. Materials and Methods

The triboelectric generators are shown schematically in Figure 1a. For the first component of the tribogenerators silicon substrate was used. A thermal oxide of 100 nm was grown on silicon wafers followed by the removal of the SiO<sub>2</sub> layer from the backside. Aluminum evaporation was performed at the backside for ohmic contact creation. Subsequently, a CQD film was deposited on the wafer. The CQDs were synthesized by microwave-assisted pyrolysis of an aqueous mixture of Citric Acid and Urea in a conventional microwave oven. Single or multiple layers of two different aqueous solutions of CQDs (10 and 20 mg/mL *w/v*) were spin-coated on the SiO<sub>2</sub> surface, followed by thermal annealing in N<sub>2</sub> gas atmosphere. The second component of the tribogenerator consisted of a Kapton surface with aluminum deposited at the back side.

The tribocharging process was carried out using the experimental setup shown in Figure 1b. The samples were tested in sliding mode with the Kapton surface rigidly attached on the setup. The sliding motion was provided by an external servomotor (Figure 1b). The parameters that can be controlled with the experimental setup include contact force, sliding velocity and oscillation mode. For the current experiments one component of the tribogenerator was subjected to a harmonic oscillation with frequency set at 3 Hz. The output voltage was monitored as a function of time using an oscilloscope. In addition, the tribogenerators were connected to a voltage quadrupler circuit to rectify and multiply the output signal in order to make it compatible with the storage device (capacitor). The charging of the capacitor was also monitored as a function of time.

Temperature and relative humidity were also measured during the experiments with the use of a thermo-hygrometer, with values ranging between 24–27 °C and 27–62% RH respectively, in order to identify the influence of the environmental parameters. All data presented in this work correspond to similar environmental conditions.



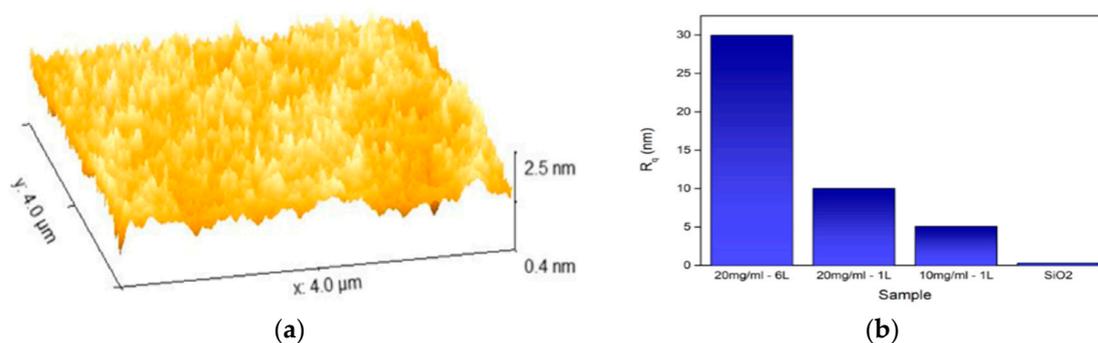
**Figure 1.** (a) Schematic illustration of the structure of the TEG and (b) photograph of the experimental setup.

## 3. Results and Discussion

As-synthesized CQDs were characterized for their morphology, as well as for the functional groups decorating their surface. High Resolution Transmission Electron Microscopy (HRTEM) revealed their quasi-spherical shape, with a diameter ranging between 2 nm–7 nm, revealing their

graphitic core with characteristic d-spacing ascribed to (1010) graphite crystallographic plane. FT-IR and EDS spectra confirmed the successful N-doping of CQDs as well as the existence of organic functional groups such as carbonyls, hydroxyls and carboxyls, which are responsible, among other properties, for their hydrophilic nature.

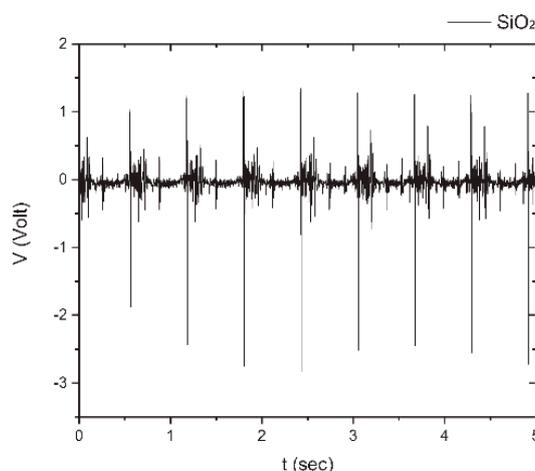
Three types of samples were tested, with varying CQD concentration and number of spin-coated layers. During the spin-coating process CQD aggregates formed, affecting the surface roughness of the samples. By varying the concentration or the number of the deposited layers we were able to fabricate samples of different surface roughness. The surface roughness (Figure 2a) was estimated by Atomic Force Microscopy (AFM) as Root-Mean-Square Roughness ( $R_q$ ). The results revealed that roughness increases with the number of deposited layers as well as with the concentration of the CQDs in the aqueous solutions, as displayed in Figure 2b.



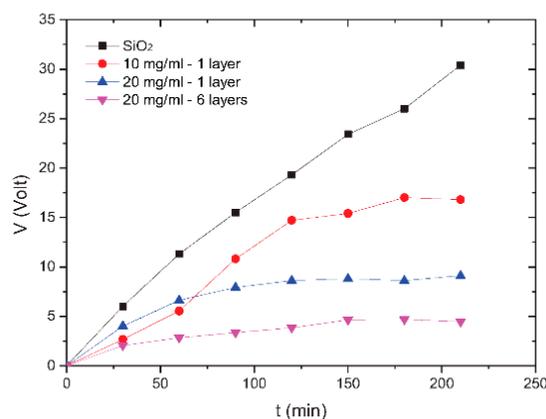
**Figure 2.** (a) AFM image of the CQD surface and (b) Surface roughness ( $R_q$ ) for the various samples.

A set of experiments was designed and carried out to study the triboelectric properties of CQDs. In the first set of experiments, we investigated the time dependence of the voltage output ( $V_{out}$ ) of the triboelectric generator for continuous sliding motion. The time dependence experiments displayed the expected periodic signal attributed to the sliding motion and an increase of the peak-to-peak voltage amplitude with time, until a saturation point was reached (Figure 3).

In the second set of measurements, the tribogenerator was connected to a voltage quadrupler circuit in order to charge a capacitor. Charging of the capacitor was performed for a total of 210 min with a rate of 30 min per measurement. Comparing the obtained charging curves, reveals that increasing the CQD solution concentration leads to decreased voltage across the capacitor. Moreover, increase of the number of layers for the same CQD concentration, results in lower capacitor voltage values (Figure 4).



**Figure 3.** Time dependent signal of a triboelectric generator for successive sliding.



**Figure 4.** Charging of the capacitor as a function of time for the different surface modifications.

The above results suggest a correlation between the roughness of the surfaces (Figure 2b) and the output voltage of the TEGS, as it appears that the increase of the surface roughness lowers the measured voltage. This is in agreement with theoretical approaches suggested in the literature, where an increase in roughness above a certain point leads to a reduction of the number of contact points between the two surfaces and subsequently to decreased triboelectrical charges [3].

At the same time, theoretical studies for sliding mode TEGS suggest that an increase in film thickness (as is expected for samples deposited with six layers of CQDs compared to one layer) also leads to an increase in the voltage output, without accounting for the roughness of the surfaces [4]. Assuming that the dielectric constant remains the same for the samples with the same CQD concentration (20 mg/mL *w/v*), we would expect a higher output voltage for the six layer sample, than for the single layer. However, our experimental data show the opposite trend, indicating that the charging mechanism induced by the surface roughness compensates the opposite trend (increasing film thickness) that is predicted in the theoretical model.

There are yet other factors affecting the triboelectric phenomenon which need to be taken under consideration in future studies. Such examples are the effects of ambient temperature and humidity as well as the electrical properties of CQDs which, given their complex structure and the plethora of trap states introduced by the various functional groups and lattice defects, are still ambiguous and under investigation. Investigation of these parameters will lead to a better understanding of the influence of surface roughness as well as the triboelectric mechanisms and the influence of CQDs.

#### 4. Conclusions

The triboelectric properties of CQDs were investigated by fabricating TEGS and characterizing them for their output signal in sliding mode. The experimental results suggest that the output voltage decreases with increasing film roughness. This provides evidence for the strong effect of surface roughness on the triboelectric phenomenon, while it also appears that its contribution to the effect is sufficient to counter the effects of other parameters, such as dielectric film thickness, the role of which, in the triboelectric phenomenon, has already been well-described in the literature.

**Author Contributions:** V.P. fabricated the devices and performed the experiments, A.S. (Antigoni Siaraka) and A.G. contributed to the measurements, A.S. (Apostolos Segkos) performed the synthesis and characterization of CQDs and contributed to device fabrication, A.B. contributed to AFM characterization, N.B. contributed to data analysis, C.T. conceived and supervised the work. All authors discussed the results and contributed to manuscript preparation.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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